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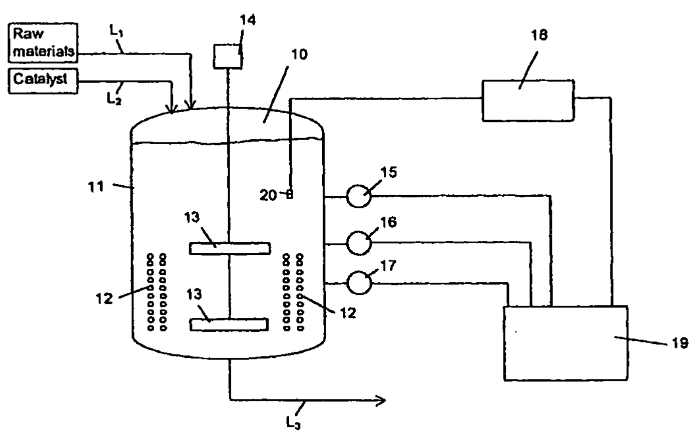
(54) Title: METHOD AND APPARATUS FOR DETERMINING VISCOELASTIC PROPERTIES OF PROCESS FLUIDS AND ITS USE



(57) Abstract

The invention relates to a method for determining viscoelastic properties of process fluids in a polymerization process. In the method at least one sensor head (20) is inserted in contact with a process fluid. The electric response of the sensor head (20) is measured and the viscoelastic properties of the process fluids are determined from the measured electric quantities. The invention also relates to an apparatus for determining viscoelastic properties and their changes of process fluids in a polymerization process. The apparatus is a sensor device comprising at least one sensor head (20), which comprises at least one thickness shear mode (TSM) resonator. The resonator is optionally shielded with a coating of corrosion resistant material and is fixed into the sensor head (20) with at least one elastic gasket. The apparatus also comprises a data sampling and processing unit (18) for the test signal generation and response measurement and processing.

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Method and apparatus for determining viscoelastic properties of process fluids and its use

The invention relates to a method for determining viscoelastic properties, especially changes in the viscoelastic properties of process fluids in a polymerization process.

The invention also concerns an apparatus for determining the viscoelastic properties and changes in these properties of polymerization process fluids processed in a polymerization reactor.

The present invention is especially related to on-line measurement of changes in molecule composition and to the on-line measurement of viscoelastic properties of polymerization fluids, particularly polymerization fluids of polyesters and adhesive resins.

Viscoelastic properties of process fluids in polymerization processes can be used as measures in describing the state of the polymerization. To these viscoelastic properties affect e.g. the degree of polymerization, i.e. the molecule composition and process fluids, the molecular weight or relative molecular weight of polymers and polymer process fluids.

Resin adhesives are generally manufactured in a batch process by an exothermal condensation reaction. The process is controlled by adjusting the temperature so that the process fluid is kept in certain constant temperatures until the desired polymerization degree has been reached. After that the process is terminated by a rapid cooling.

It is known from the prior art that in the polymerization processes there is a need for sensors and measurement equipment for controlling proceeding of the reaction and

quality of the final product. Typical measurement parameters are such as temperature and pressure. Sensors make it possible to adjust the process parameters on-line.

In the polymerization process the cut-off point (COP) is the exact point of time when the product has reached desired properties such as a desired molecule weight. The reaction in the reactor is then cut off and the process fluid is cooled. In the prior art the determination of the cut-off point of the polymerization process, particularly in the batch reactors, is carried out by taking process fluid samples from the reactor and analyzing the samples in a laboratory. A series of samples is needed to predict the time when the process can be cut off. In this method the cut-off point (COP) is always a prediction or a guess. This causes deviations in the quality of the final product.

A feasible and economical method for monitoring on-line the polymerization in the resin production is not taught or suggested in the prior art. A particular problem in the sensors and technique known from the prior-art is the placement of the sensor device inside the polymerization reactor, where it will be in contact with the process fluids. The reactor temperature, corrosion, deterioration and contamination of the sensor device caused by process fluids have caused insurmountable problems when applying the mechanical, optic or electrical viscometers to the process follow-up.

A thickness shear mode (TSM) resonator typically comprises a thin disk of AT-cut quartz and electrodes on both sides. The fundamental resonance frequency of such a device typically lies in megahertz range. Because of the piezoelectric coupling in quartz, the shear stress at resonator surface and the resonator electric impedance are strictly related to each other. This results in the fact that the near resonance electric response of a TSM resonator reacts very sensitively to the viscoelastic changes in the media adjacent to the resonator surface and gives one means to monitor these changes.

From the prior art a method and an apparatus for determining the density and viscosity of the newtonian fluids of low molecule weight using near resonance electric

response of a TSM resonator is known. It is not known to use the method with non-newtonian polymeric fluids. It is not known to use this measurement system for measuring characteristics of polymers.

Further, it is not known to place any TSM resonator sensor apparatus into a polymerization reactor. It is not known to monitor the viscoelastic changes in a polymerization process with a TSM resonator sensor apparatus placed inside a reactor.

With respect to the prior art most closely related to the equipment according to the present invention, reference is made to the following articles.

The use of TSM resonators for measuring properties of some fluids or processes is known from the *US patents US 5,661,233, US 5,734,098 and US 5,201,215.*

US 5,661,233 introduces an acoustic-wave sensor, where a TSM resonator is a possible sensing part for analyzing properties of petroleum-based composition. The apparatus and method are used for measuring cloud point, pour point and/or freeze point and it can be used in recover transport, storage, refining and use of petroleum and petrolem-based products. *US 5,734,098* introduces a method which uses a TSM resonator for measuring mass deposition and fluid properties in petroleum processing, petrochemical and water treatment systems. *US 5,201,215* discloses a method using a TSM resonator to determine total mass of a solid and physical properties of a fluid.

The object of the present invention is to provide a novel method for determining on-line viscoelastic properties and changes in these properties of process fluids in a polymerization process.

The object of the present invention is to provide a novel method for determining the degree of polymerization and the cut-off point of the reaction carried out in the polymerization reactor.

The particular object of the present invention is to provide a novel method for determining the cut-off point of the reaction in the polymerization batch reactor.

In view of achieving the objectives stated above and those that will come out later, the method according to the invention is mainly characterized in that it comprises the steps of:

— inserting at least one sensor head in contact with a process fluid, the sensor head comprising at least one thickness shear mode (TSM) resonator comprising at least one piezoelectric crystal, and electrodes, the resonator being shielded on at least that side, which is in contact with process fluids, with a coating or coatings of corrosion resistant material, and the resonator being fixed into the sensing head with at least one elastic gasket in order to allow only the corrosion resistant coating or coatings to be in contact with the process fluids,

— measuring the electric response of the TSM resonator at a frequency range near the fundamental or a harmonic resonance of the TSM resonator,

— determining from the measured electric quantities the viscoelastic properties of the process fluids.

The apparatus according to the invention is mainly characterized in that the apparatus is a sensor device comprising:

— at least one sensor head placed inside the polymerization reactor, said sensor head comprising at least one thickness shear mode (TSM) resonator, which comprises at least one piezoelectric crystal, and electrodes, the resonator being optionally shielded with a coating or coatings of corrosion resistant material, and being fixed into the sensing head with at least one elastic gasket, and

— a data sampling and processing unit for test signal generation and response measurement and processing.

In a preferred embodiment the apparatus is placed in a reactor, where the process, preferably a polymerization process is carried out, and that the resonator is shielded on at least that side, which is in contact with the process fluid with a coating or coatings of corrosion resistant material.

The resonator is fixed with at least one electric gasket in order to allow only the corrosion resistant coating or coatings to be in contact with the process fluids in said polymerization reactor.

The signals from TSM resonator are transferred into a data sampling and processing unit, where test signal generation and response measurement and processing occurs.

The advantage of the present invention is to determine the cut-off point of the polymerization process accurately. This reduces essentially the fluctuation of quality of the final product from batch to batch. This way there is no more need to adjust afterwards the properties of the final product to the desired values. Also the pass time of a batch will become shorter and therefore the production capacity and efficiency will improve.

A further advantage of the invention derives from the simple structure of a TSM resonator and the sensor head. The polished coated quartz is chemically durable, it is not vulnerable to contamination and is easily cleaned when needed. Further, the sensor device can be provided with a microbalance function which reveals contamination. Therefore an automatic cleaning function can be incorporated to the sensor device according to the invention.

In the following, the invention will be described in detail with reference to the figures in the accompanying drawing, the invention being, however, by no means strictly confined to the details of said embodiments or variations.

Figure 1 is a schematic illustration of a batch reactor containing the apparatus according to the invention for measuring the viscoelastic properties of polymer fluids and changes in these properties in polymerization processes.

Figure 2 is a cross-section illustration of the sensor head of the sensor apparatus according to the invention.

Figure 3 shows an example of a batch process follow-up and cut-off point determination using both the conventional efflux time measurement and the sensor device according to the invention.

Fig. 1 shows a schematic illustration of a batch reactor 10 equipped with the apparatus for measuring viscoelastic properties of polymers according to the invention. The raw materials are charged to the reactor 10 via the line L_1 and the catalyst via line L_2. The final product is taken out of the reactor 10 via the line L_3. Inside the reactor vessel 11 there are cooling coils 12 and the impellers 13 of the agitator 14. Sensor devices for measuring the state of the process are located inside the reactor 10 engaged to the reactor vessel 11. In this example the reactor 10 is equipped with a temperature sensor 15, pressure sensor 16, weight sensor 17 and sensor head 20 for measuring viscoelastic properties and their changes according to the invention. The sensor head 20 is connected to the data sampling and processing unit 18 and the signal is then transferred to the process control unit 19. Temperature signal from the temperature sensor 15, pressure signal from the pressure sensor 16 and weight signal from the weight sensor are transferred to the process control unit 19, too.

Fig. 2 shows a cross section illustration of the sensor head 20 according to the invention. The sensing part of the sensor head 20 is a TSM resonator comprising the piezoelectric crystal 21 and electrodes 22,23.

The electrical lead between the process side electrode 22 and the sensor shell 24 is constructed by using an electrically conductive gasket ring 26 or by using an electrically

non-conductive gasket and gold threads or a strip of electrically conductive adhesive tape or metal foil 28. The wire 29 is connected to the upper electrode 23 with electrically conductive glue, or the wire 29 itself can be a strip of electrically conductive adhesive tape or metal foil.

According to the invention the proceeding of polymerization processes is monitored by electrical response of the TSM resonator 21,22,23 at a range of frequencies near the fundamental or a harmonic resonance of the resonator. The electrical response to be measured can be the admittance spectrum, the admittance magnitude maximum, the half band width of the admittance magnitude spectrum, the resonance frequency or any other electrical quantity that describes the resonator characteristics. Essentially the quantities should be related to the changes in the dissipation and storage of the resonator power and, therefore, to the viscoelastic changes adjacent to the resonator surface. The test signal generation and the response signal measurement and processing are carried out by the data sampling and processing unit 18.

The TSM resonator 21,22,23 is shielded in this embodiment on both sides with corrosion resistant layers 36,37. The corrosion resistant material can be the electrode metal itself such as gold, titanium, or platinum or some other material such as diamond like coating (DLC) or titanium nitride. The outer corrosion resistant layer 36 comes to the process side and the inner corrosion resistant layer 37 is inside the sensor head 20. To achieve durable and stable enough structure the TSM resonator 21,22,23 is engaged to the shell 24 with elastic gaskets 25,26. The shell 24 is preferably constructed of corrosion resistant metals, like stainless steel, titanium or other corrosion resistant metal alloys.

The shell 24 has an opening to the process fluid so that only the outer corrosion resistant layer 36 of the TSM resonator 21,22,23 comes in contact with the process fluid. The supporting lid 27 is placed between the shell 24 and the inner coating layer 37 so that it supports tightly the TSM resonator 21,22,23 to the shell. The supporting lid 27 is tightened with a tightening means 31 which is preferably provided with a screw

thread. The shell lid 30 is tightly supported to the shell 24 with attachment means 32, 33 which are preferably screws.

The basic material of gaskets 25,26 can be e.g. of fluoride plastic based elastomers such as Viton® or Kalrez® (DuPont Dow Elastomers Ltd.) or of pure polytetrafluoride-ethylene. Gaskets 25,26 are preferably gasket rings or other type of elastic gaskets.

Figure 3 shows an example of a batch process follow-up and cut-off point determination using both the conventional efflux time measurement and the sensor device according to the invention. The horizontal axis presents time while the vertical axis presents process temperature (drawn as solid line), manually measured efflux time of process fluid samples (triangles along the dashed line), polymerization degree of process fluids (triangles along the solid line), and a quantity constructed from the near resonance electric response of a TSM resonator installed into a contact with process fluid inside the reactor (dotted line). All numerical values are presented in an arbitrary scale. Polymerization degree as mentioned above is measured by gel permeation chromatography (GPC).

The temperature curve in Fig. 3 represents a typical resin batch process. The process temperature is first risen to a certain level and kept there. After a certain time the process is driven to a lower temperature level in order to slow down the polymerization and achieve enough time to perform the efflux time measurements and cut-off point (COP) extrapolation. Finally, when the cut-off point is reached the process is terminated by a rapid cooling.

The conventional process follow-up is carried out by measuring the efflux-time of process fluid samples taken out of the reactor. The samples are first transferred into a laboratory where they are cooled to room temperature. Then the efflux time of the sample is measured. A series of samples is needed to extrapolate the cut-off point, the exact time when the process fluid has reached a pre-determined room temperature efflux time cut-off level. This extrapolation is presented in Fig. 3.

The output of the TSM resonator sensor device is presented with the dotted line (on-line COP). The output is constructed by i) measuring, at a frequency range near the fundamental resonance of the resonator, the change in the TSM resonator impedance magnitude minimum (admittance magnitude maximum) in respect to the value measured on the resonator in contact with water ii) taken the square of the measured quantity. It is known from the prior art that the output constructed, in the case of low-viscosity Newtonian fluids, would be proportional to the change in the viscosity-density product of the fluid.

The output of the TSM resonator sensor device was recorded during fifty industrial resin production batches. In all batches, the sensor output had the same presented shape and signal level. Without any exception, the sensor device output increased during both isothermal process phase. The collected data showed a correlation between the sensor device output and manual efflux time measurements and established the fact that the sensor device output can be utilised in the process cut-off point determination.

When applied to polymerization process follow-up, the sensor device according to the invention has several advantages over the conventional laboratory method. Firstly, on-line information of the process state is given - there is no delay due the transfer, cooling and efflux time measurement of the process fluid sample. Secondly, the extrapolated cut-off point is replaced by an accurate real-time measurement. As a consequence, the quality of the final product is improved. The invention also enables one to control polymerization processes at higher temperatures longer than before, which can result in shortened process durations. Moreover, there is no need to the time consuming and dangerous manual process fluid sampling any more.

The method and the apparatus according to the invention are used for measuring the viscoelastic properties and their changes of polymers, polyester resins or adhesives and for determining the cut-off point of adhesive resin batch processes. The method and the apparatus are especially well suited for this reactor type but they can be adapted to the other types of polymerization reactors as well, such as the continuous loop reactors. The apparatus according to the invention can also be placed inside a sampling loop of a

polymerization reactor. The method and the apparatus according to the invention can also be used for the follow-up of the molecule composition of the process fluid in the polymerization reactors and for controlling the polymerization reactor.

In the following, the patent claims will be given, and various details of the invention may show variation within the scope of the inventive idea defined in the patent claims and differ from the details disclosed above for the sake of example only.

Patent claims

1. A method for determining viscoelastic properties of process fluids in a polymerization process, **characterized in** that it comprises the steps of:

— inserting at least one sensor head (20) in contact with a process fluid, the sensor head (20) comprising at least one thickness shear mode (TSM) resonator comprising at least one piezoelectric crystal (21), and electrodes (22,23), the TSM resonator (21,22,23) optionally being shielded with a coating (36) or coatings (36,37) of corrosion resistant material, and the resonator (21,22,23) being fixed into the sensor head (20) with at least one elastic gasket (25,26),

— measuring the electric response of the TSM resonator (21,22,23) at a frequency range near the fundamental or a harmonic resonance of the TSM resonator (21,22,23), and

— determining from the measured electric quantities the viscoelastic properties of the process fluids.

2. A method according to claim 1, **characterized** in that viscoelastic properties and their changes of polymerization process fluids processed in polymerization reactors are measured.

3. A method according to claim 1 or 2, **characterized** in that the admittance spectrum of the TSM resonator (21,22,23) at a frequency range near the fundamental or a harmonic resonance of the TSM resonator (21,22,23) is measured.

4. A method according to any of claims 1 to 3, **characterized** in that the sensor head (20) is placed in a reactor, where the polymerization process is carried out, and that the TSM resonator (21,22,23) is shielded on at least that side, which is in contact with the process fluid with a coating (36) or coatings (36,37) of corrosion resistant material.

5. A method as claimed in any of claims 1 to 4, **characterized** in that the maximum value of the electric admittance magnitude at a frequency range near the fundamental or a harmonic resonance of the TSM resonator (21,22,23) is measured.

6. A method as claimed in any of claims 1 to 5, **characterized** in that the value of the fundamental or a harmonic resonance frequency of the TSM resonator (21,22,23) is measured.

7. A method as claimed in any of claims 1 to 6, **characterized** in that the value of the half band width of the electric admittance magnitude spectrum of the TSM resonator (21,22,23) is measured.

8. A method according to any of claims 1 to 7, **characterized** in that the electric quantity to be measured describes the TSM resonator characteristics that are affected by viscoelastic changes in the fluid adjacent to the resonator surface.

9. A method as claimed in any of claims 1 to 8, **characterized** in that the near resonance electric response of said TSM resonator (21,22,23) is measured continuously providing an on-line determination of viscoelastic properties of the process fluids during the polymerization process.

10. A method according to any of claims 1 to 9, **characterized** in that the signals from said TSM resonator (21,22,23) are transferred into a data sampling and processing unit (18).

11. A method as claimed in any of claims 1 to 10, **characterized** in that the degree of polymerization and the cut-off point of the polymeriza-tion process are determined on-line by using the data of the on-line determination of viscoelastic properties of the polymerization process fluids.

12. A method as claimed in any of claims 1 to 11, **characterized** in that the products to be prepared in the polymerization reactor (10) are preferably polyester resins or adhesives, such as formaldehyde resins.

13. A method as claimed in any of claims 1 to 12, **characterized** in that viscoelastic properties and their changes of the process fluids during the polymerization process are determined in batch reactors.

14. A method as claimed in any of claims 1 to 12, **characterized** in that viscoelastic properties and their changes of the process fluids during the polymerization process are determined in loop reactors.

15. An apparatus for determining viscoelastic properties and their changes of process fluids in a polymerization process, **characterized** in that the apparatus is a sensor device comprising:

— at least one sensor head (20), comprising at least one thickness shear mode (TSM) resonator, which comprises at least one piezoelectric crystal (21), and electrodes (22,23), the thickness shear mode (TSM) resonator (21,22,23) being optionally shielded with a coating (36) or coatings (36, 37) of corrosion resistant material, and being fixed into the sensor head (20) with at least one elastic gasket (25,26), and

— a data sampling and processing unit (18) for the test signal generation and response measurement and processing.

16. An apparatus as claimed in claim 15, **characterized** in that the thickness shear mode (TSM) resonator comprises one piezoelectric crystal (21) and electrodes (22,23).

17. An apparatus as claimed in claim 15 or 16, **characterized** in that the elastic gasket (25,26) is of an elastomer.

18. An apparatus as claimed in any of claims 15 to 17, **characterized** in that the elastic gasket (25,26) is an elastic gasket ring.

19. An apparatus according to any of claims 15 to 18, **characterized** in that the sensor head (20) is placed in a reactor, where the polymerization process is carried out, and that the TSM resonator (21,22,23) is shielded on at least that side, which is in contact with the process fluid with a coating (36) or coatings (36,37) of corrosion resistant material.

20. An apparatus as claimed in any of claims 15 to 19, **characterized** in that the TSM resonator (21,22,23) is shielded on both sides with a corrosion resistant layer coating (36,37).

21. An apparatus as claimed in any of claims 15 to 20, **characterized** in that the corrosion resistant material is of the electrode metal itself preferably of gold, titanium or platinum or some other material such as diamond like coating (DLC) or titanium nitride.

22. An apparatus as claimed in any of claims 15 to 21, **characterized** in that the said TSM resonator (21,22,23) is separated from the process fluid with an elastic gasket (25, 26) in order to allow only the corrosion resistant coating (36) to be in contact with the process fluid.

23. An apparatus as claimed in any of claims 15 to 22, **characterized** in that the sensor head (20) is placed inside a polymerization batch reactor.

24. An apparatus as claimed in any of claims 15 to 22, **characterized** in that the sensor head (20) is placed inside a polymerization loop reactor.

25. An apparatus as claimed in any of claims 15 to 22, **characterized** in that the sensor head (20) is placed inside a sampling loop of a polymerization reactor.

26. Use of the method according to the claims 1 to 14 for monitoring viscoelastic properties of the polymerization process fluids processed in a polymerization reactor.

27. Use of the method according to the claims 1 to 14 for controlling the quality of the final product in a polymerization reactor.

28. Use of the method according to the claims 1 to 14 for the on-line determination of the degree of polymerization of polymers to be polymerized.

29. Use of the method according to claim 28 for the on-line determination of the degree of polymerization of polyesters and adhesive resins, such as formaldehyde resins, during the polymerization process.

30. Use of the method according to claims 1 to 14 for the on-line determination of the cut-off point of the polymerization process.

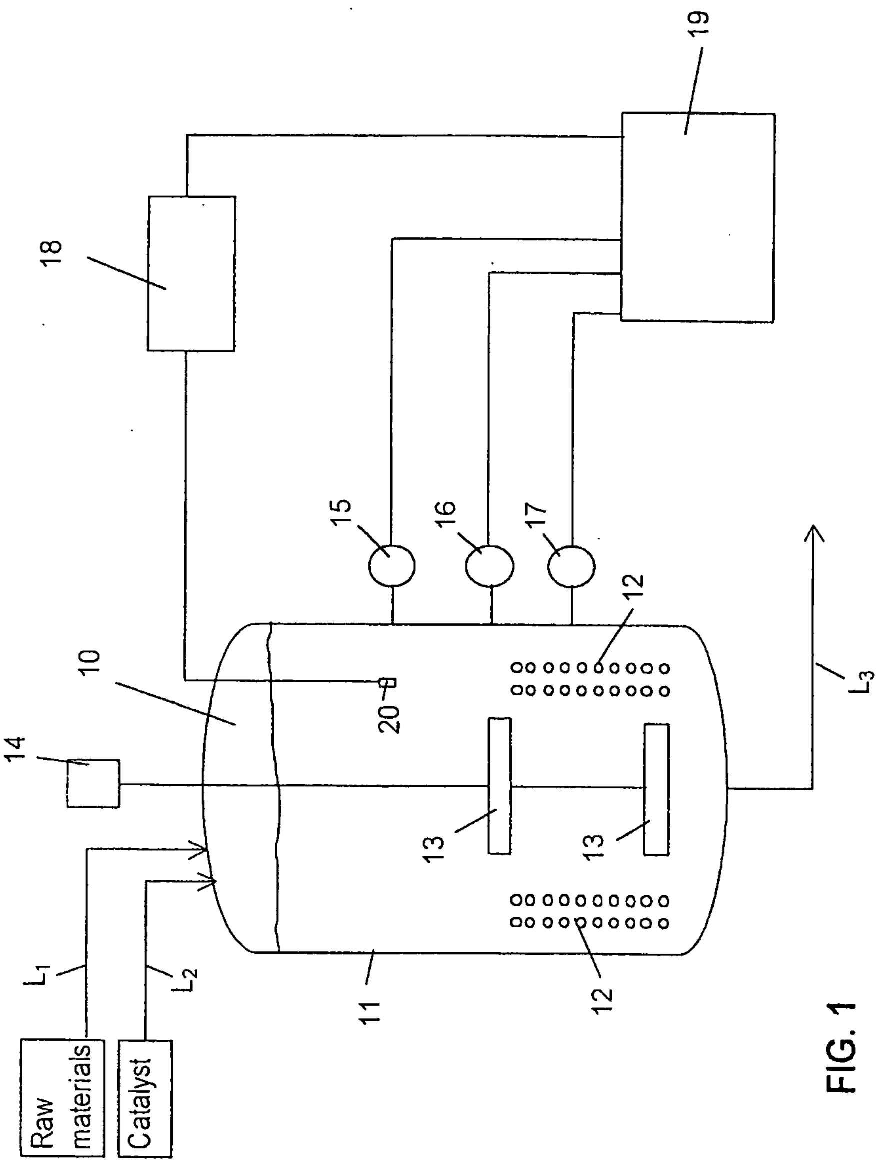
19
18
15
16
17
12
10
20
14
13
13
12
L_1
L_2
L_3
11
Raw materials
Catalyst

FIG. 1

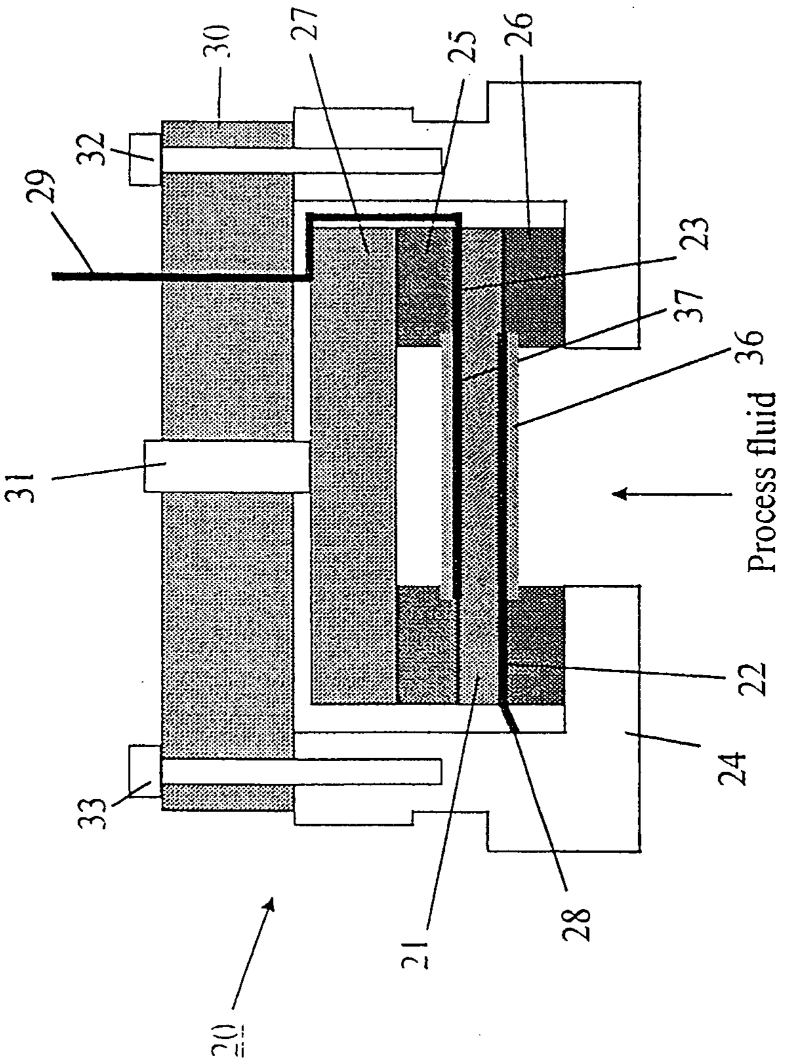

FIG. 2

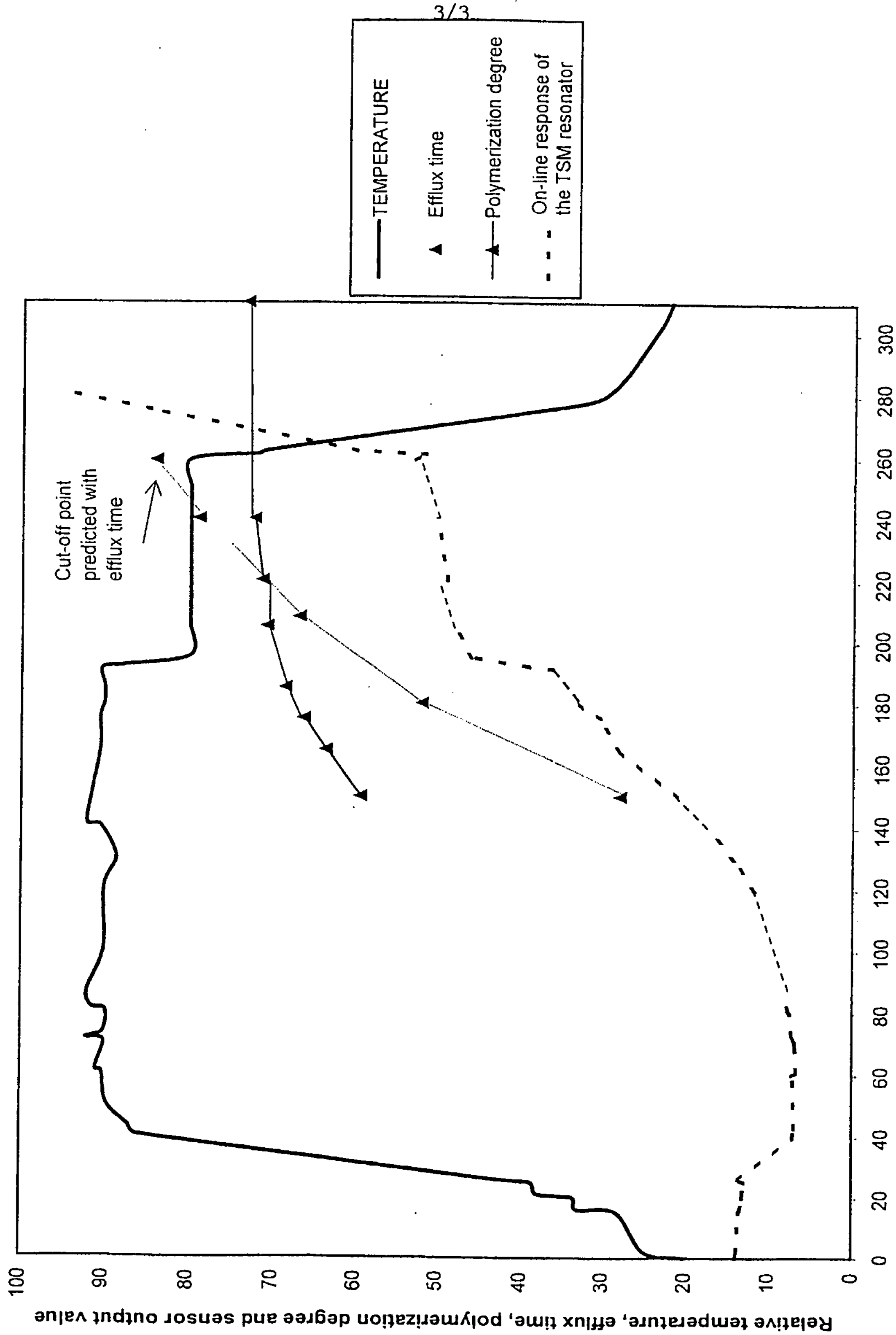
TEMPERATURE
Efflux time
Polymerization degree
On-line response of the TSM resonator
Cut-off point predicted with efflux time
Relative temperature, efflux time, polymerization degree and sensor output value
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300

FIG. 3

1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 99/00983

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: G01N 11/16, G01N 33/44
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC,PAJ,WPI,IEL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 2049672 A (DEUTSCHE TEXACO AG), 13 April 1972 (13.04.72), page 1, line 1 - line 10; page 3, line 29 - page 4, line 8 --	1-30
Y	US 4741200 A (R.H.HAMMERLE), 3 May 1988 (03.05.88), column 2, line 3 - line 25; column 3, line 15 - line 46, claim 1 --	1-30
A	US 4778765 A (F-M.BOLLENRATH ET AL), 18 October 1988 (18.10.88), abstract --	1-30

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 March 2000	24-03-2000
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 99/00983

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